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CHARACTERISTICS OF VANADIUM DOPED AND BAMBOO ACTIVATED CARBON COATED LiFePO_4 AND ITS PERFORMANCE FOR LITHIUM ION BATTERY CATHODE

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ABSTRACT

CHARACTERISTICS OF VANADIUM DOPED AND BAMBOO ACTIVATED CARBON COATED LiFePO_4 AND ITS PERFORMANCE FOR LITHIUM ION BATTERY CATHODE. Vanadium doped and bamboo activated carbon coated lithium iron phosphate (LiFePO_4) used for lithium ion battery cathode has been successfully prepared. Lithium iron phosphate was prepared through a wet chemical method followed by a hydrothermal process from the starting materials of LiOH , $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The dopant variations of 0 wt.%, 3 wt.%, 5 wt.%, and 7 wt.% of vanadium and a fixed 3 wt.% of bamboo activated carbon were carried out via a solid-state reaction process each by using NH_4VO_3 as a source of vanadium and carbon pyrolyzed from bamboo tree, respectively. The characterization was carried out using X-ray Diffraction (XRD) for the phase formed and its crystal structure, Scanning Electron Microscope (SEM) for the surface morphology, Electrochemical Impedance Spectroscopy (EIS) for the conductivity, and battery analyzer for the performance of lithium ion battery cathode. The XRD results show that the phase formed has an olivine based structure with an orthorhombic space group. Morphology examination revealed that the particle agglomeration decreased with the increasing level of vanadium concentrations. Conductivity test showed that the impedance of solid electrolyte interface decreased with the increase of vanadium concentration indicated by increasing conductivity of $1.25 \times 10^{-5} \text{ S/cm}$, $2.02 \times 10^{-5} \text{ S/cm}$, $4.37 \times 10^{-5} \text{ S/cm}$, and $5.69 \times 10^{-5} \text{ S/cm}$, each for 0 wt.%, 3 wt.%, 5 wt.%, and 7 wt.% vanadium, respectively. Vanadium doping and bamboo activated carbon coating are promising candidate for improving lithium ion battery cathode as the initial charge and discharge capacity at 0.5C for LiFePO_4/C at 7 wt.% vanadium is in the range of 8.0 mAh/g.

Keywords : Activated carbon, Bamboo, LiFePO_4 , Lithium ion battery

ABSTRAK

SIFAT-SIFAT LiFePO_4 YANG DIDOPING VANADIUM DAN BERLAPIS KARBON AKTIF DARI BAMBU SERTA KINERJANYA SEBAGAI KATODE BATERAI ION LITIU. Dalam penelitian ini, bahan aktif litium besi fosfat (LiFePO_4) yang didoping vanadium dan berlapis karbon yang dipirolisis dari bambu untuk katode baterai ion litium telah berhasil dibuat. Bahan LiFePO_4 disiapkan melalui metode kimia basah yang diikuti proses hidrotermal dari bahan awal LiOH , $\text{NH}_4\text{H}_2\text{PO}_4$, dan $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Penambahan variasi 0 %berat, 3 %berat, 5 %berat, dan 7 %berat vanadium dan 3 %berat karbon dilakukan melalui proses reaksi padatan masing-masing menggunakan reagen NH_4VO_3 sebagai sumber vanadium dan arang yang dipirolisis dari bambu. Proses karakterisasi dilakukan menggunakan Difraksi Sinar-X (XRD) untuk melihat fase yang terbentuk dan strukturnya, Mikroskop Elektron (SEM) untuk melihat morfologi permukaan, Spektroskopi Impedansi Elektrokimia (EIS) untuk menguji konduktivitas, dan pengujian baterai untuk melihat aktivitas dan kinerja bahan sebagai katode baterai ion litium. Hasil pengujian XRD memperlihatkan bahwa fase yang terbentuk memiliki struktur dasar olivin dengan grup ruang ortorombik. Pengujian morfologi memperlihatkan bahwa aglomerasi partikel semakin berkurang dengan naiknya konsentrasi vanadium. Pengujian konduktivitas memperlihatkan bahwa impedansi antarmuka padat-elektrolit semakin berkurang dengan naiknya konsentrasi vanadium yang dibuktikan naiknya konduktivitas sekitar $1,25 \times 10^{-5} \text{ S/cm}$; $2,020 \times 10^{-5} \text{ S/cm}$; $4,371 \times 10^{-5} \text{ S/cm}$; dan $5,69 \times 10^{-5} \text{ S/cm}$, masing-masing untuk 0 %berat, 3 %berat, 5 %berat, dan 7 %berat vanadium. Penambahan vanadium dan pelapisan dengan karbon dari hasil pirolisis bambu ini memiliki potensi untuk meningkatkan kinerja katode baterai ion litium dimana kapasitas charge dan discharge awal dari bahan pada 0,5C mampu mencapai 8,0 mAh/g untuk LiFePO_4/C pada 7 %berat vanadium.

Kata kunci : Karbon aktif, Bambu, Litium besi fosfat, Baterai litium

INTRODUCTION

With the cumulative problems of global warming due to the use of non-renewable fossil based fuels, many efforts have been made to replace this non-renewable fossil fuels with other sustainable and green energy sources such as solar, wind, and hydroelectric power (Mathew et al. 2014). Unfortunately, these sources are uncontrollable and intermittent in nature, which then brings a great research interest in material development for energy storage (Y. D. Zhang et al. 2015). Lithium Ion Battery (LIB) is one of the devices developed for this purpose.

The electrochemical performance of cathode materials is very important in determining the property of LIBs, however, the current cost is still nearly twice as much as the anode that make the research about the developments and optimizations of the cathode active materials have never ended (Y. D. Zhang et al. 2015). LiFePO_4 is the most promising cathode material because of its excellent cyclic stability, non-toxic, environmental friendliness, low cost, and high theoretical capacity of 170 mAh/g at relatively high potential (~ 3.45 V vs. Li/Li^+) (Qin, Ma, and Wang 2014). However, LiFePO_4 usually shows a poor rate capability because of its low intrinsic electronic conductivity ($\sim 10^{-9}$ S/cm) and low diffusion coefficient (Lei et al. 2015).

Carbon coating is the most promising method to improve the electronic conductivity on the surface of LiFePO_4 particles (Li et al. 2017). It has been shown that the presence of activated carbon inside these composite electrodes improves the electronic conductivity and the performance of the materials at high current density of the LiFePO_4 (Böckenfeld et al. 2012). Lithium ion diffusion can be improved by supervalent metal ion doping or substitution at Fe site of LiFePO_4 (Su et al. 2017). Vanadium substitution can significantly improve the electrochemical performance of LiFePO_4 cathode material for lithium ion battery (Chen et

al. 2015). This is true because of V doping can create a vacancy and lattice disorder in the crystal structure of LiFePO_4 , therefore Li ion can move easier between cathode materials (Chiang et al. 2012).

There are many types of bamboo found in Indonesia, one of which is a clumping bamboo called bambusa balcooa (Bystriakova et al. 2013). Many research have been performed to increase the added value of this bamboo such as using it as cheap carbon source for activated carbon (Tsubota et al. 2018) and biochar for lithium-sulfur battery (Gu et al. 2015). They found that bamboo derived carbon has the potential to be used in many applications due to its simple process and abundant source in nature.

In this work, activated carbon pyrolyzed from bamboo is used as a carbon source applied as active material coating in lithium ion battery cathode. At the same time, the influence of vanadium doping coated by this bamboo activated carbon on the electrochemical behavior of LiFePO_4 cathode material in the forms of composite $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4/\text{C}$, where $0 \leq x \leq 0.07$ has been investigated. The results obtained from the investigation are provided and discussed in detail.

MATERIALS AND METHODS

Preparation of Bamboo Activated Carbon

Old bamboo (*Bambusa balcooa*) stems with an average diameter of 10 cm were cut and chopped into small pieces and dried in an oven at 105 °C for 24 hours. The dried bamboo pieces were then heated in a furnace at 400 °C for 4 hours to form bamboo charcoals. The steps in producing this bamboo charcoal can be seen in Figure 1. The bamboo charcoals were then crushed to form charcoal powder in a ball mill and sieved into fine carbon fragments.



Figure 1. The steps in producing bamboo charcoal. Left to right is bamboo tree, pieces of bamboo internodes, chopped and dried bamboo, and bamboo charcoal

The fine carbon fragments were further activated through a chemical activation by soaking the fine bamboo carbon fragments in a closed system using 30% phosphoric acid (H_3PO_4 , E-Merck) solution with impregnation ratios of 4 : 1 (w/w) for 24 hours. The sample was then dried in an oven at 105 °C for 20 hours. The dried sample was then physically activated through a heating process at 500 °C before being neutralized using NaOH and successively rinsed with distilled water until the filtrate reached a stable pH of 7. Finally, the moisture was removed by drying the bamboo activated carbon at 105 °C for another 20 hours and ready for characterization.

Preparation of LiFePO_4

LiFePO_4 was firstly synthesized via hydrothermal method using precursors of $\text{NH}_4\text{H}_2\text{PO}_4$, LiOH, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, all of which analytical grade reagents from E-Merck. The precursors were taken as starting materials with a molar ratio of 1 : 2 : 1. The precursors were dissolved in deionized water and were mixed using a magnetic stirrer. The resulting solution was placed in a Teflon-lined stainless steel autoclave and the hydrothermal reaction was performed at 170 °C for 20 hours. The obtained product was cooled to room temperature and washed with distilled water until the pH reached 7 before being dried at 105 °C to obtain greenish color of LiFePO_4 powder.

Composite $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4/\text{C}$ Preparation

Composite $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4/\text{C}$ was fabricated through a solid-state reaction by firstly preparing the as-synthesized LiFePO_4 powders from the previous step with variations of 0 wt.%, 3 wt.%, 5 wt.%, and 7 wt.% ammonium metavanadate (NH_4VO_3 , Sigma Aldrich) and a fix amount of 3 wt.% bamboo activated carbon. LiFePO_4 powder was mixed with NH_4VO_3 in a ball mill for 20 minutes. The next, bamboo activated carbon was added into the chamber and the milling was continued until a homogeneous mixture was obtained. The ratio of LiFePO_4 , activated carbon, and NH_4VO_3 was (97-x) : 3 : x, where x = 0 wt.%, 3 wt.%, 5 wt.%, and 7 wt.%. The mixture was then sintered at 800 °C in a nitrogen atmosphere for 4 hours. Finally, the product was cooled down to room temperature and ready for the characterization.

Battery Fabrication and Testing

The $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4/\text{C}$ composite form previous process was mixed with poly(vinylidene fluoride) (PVDF, MTI) in N-methyl pyrrolidone (NMP, MTI) solvent to obtain active material. Active material was coated onto an aluminum sheet (MTI) using doctor blade and heated at 80 °C. Battery fabrication was prepared in the

form of a coin in the glove box on the split test cell using Li metal anode for half-cell using LiPF_6 as an electrolyte. The conductivity was tested through an electrochemical impedance spectroscopy, whereas the battery performance was measured using a battery analyzer.

Measurement Apparatus and Condition

X-Ray Diffraction (XRD, ARL OPTX-2050) was carried out using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 35 mA on powder specimen to characterize the structural properties of the materials. Scanning Electron Microscope (SEM, FEI Quanta-650) equipped with energy dispersive X-ray spectroscopy (EDX) was performed at 20 kV to characterize the surface morphology and elemental compositions. Electrochemical Impedance Spectroscopy (EIS, Hioki LCR 3532-50) was used to measure the conductivity of the active materials, whereas the battery performance was measured using a battery analyzer (MTI BST8-3 Battery Analyzer). All measurements were performed under ambient condition with no control on humidity and pressure.

RESULTS AND DISCUSSION

Diffraction Patterns

X-ray diffraction was carried out to confirm the phase and crystal structure of the sample and the result is given in Figure 2. As seen in Figure 2, the activated carbon from bamboo has formed indicated by dominant peaks at 2θ 26.61°, 43.45°, 46.32°, 54.81°, and 56.68° corresponding to (111), (100), (110), (222), and (211) orthorhombic crystal planes, respectively. In addition to these peaks, however, there are some other peaks formed at 2θ 15.13, 23.186, 24.16, and 31.64 corresponding to ($\bar{2}$ 02), ($\bar{1}$ 13), ($\bar{2}$ 13), and (021) monoclinic crystal planes of diphenyl acetylene, respectively. This result shows that pyrolyzing the bamboo at 400 °C and activated it of up to 500 °C has not transformed the cellulose to carbon completely. Nonetheless, quantification of the two phases revealed that more than 10% of the cellulose have been transformed to carbon. Because of that, the result was then used for further testing.

Using Scherrer's formula (Cullity 1978), it can be shown that the crystallite size of the carbon is around 35 nm. This suggests that the crystallinity of the bamboo activated carbon is relatively high. Further, the X-ray diffraction patterns of $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4/\text{C}$ composite are given in Figure 3. As seen in Figure 3, all of diffraction patterns of the samples are in agreement with that of LiFePO_4 reference with a structure crystal indexed to olivine structure of Pnma orthorhombic (JCPDS No.083-2092)..

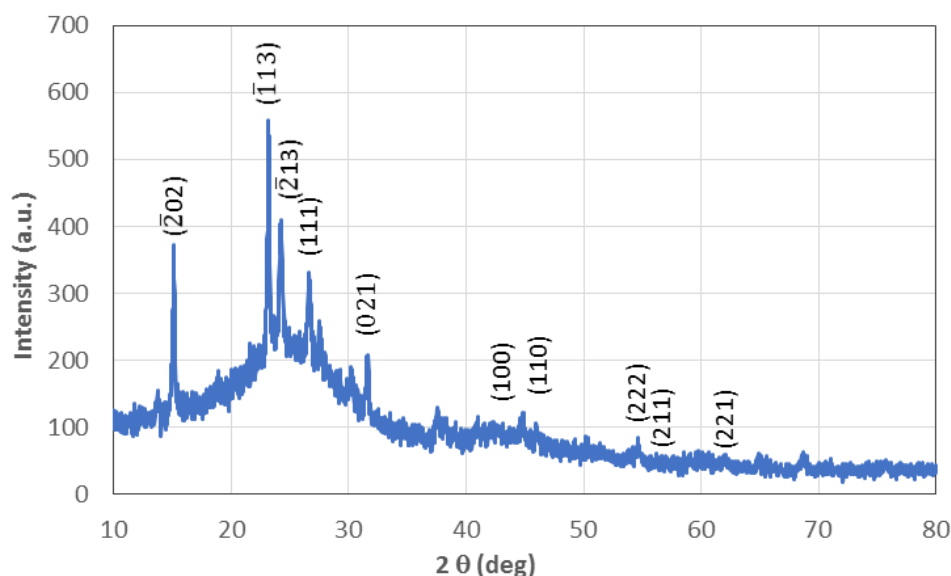


Figure 2. X-ray diffraction pattern of bamboo activated carbon pyrolyzed at 400 °C

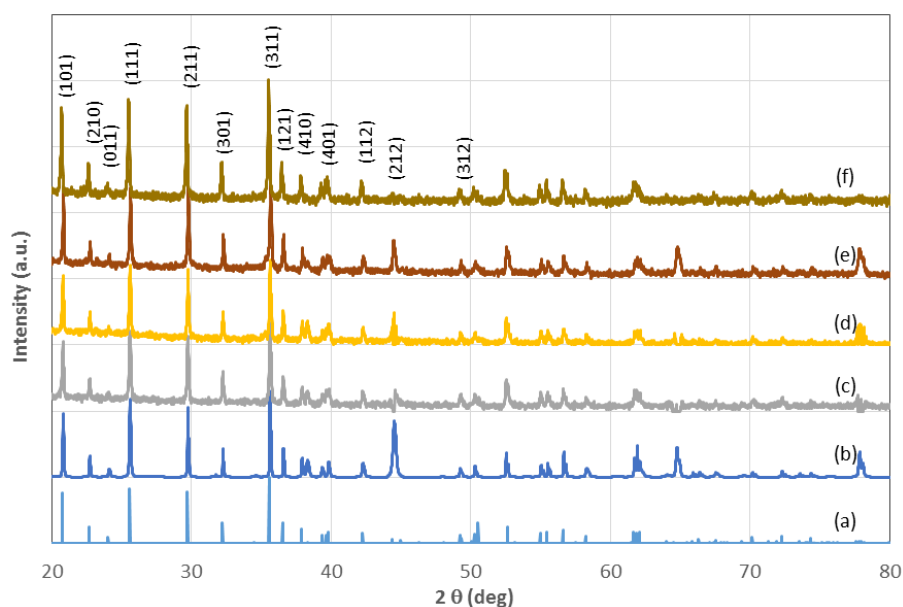


Figure 3. X-ray diffraction pattern of (a) reference, (b) commercial LiFePO_4 , (c) as-synthesized LiFePO_4 , (d) LiFePO_4 3 wt.% vanadium, (e) LiFePO_4 5 wt.% vanadium, and (f) LiFePO_4 7 wt.% vanadium

No other peak appears for crystallized carbon because of the small amount and the carbon contained is dominated of amorphous phase of acetylene or not enough crystallized phase exists to be detected by XRD (Long et al. 2015). The carbon in this composite does not affect the structure of LiFePO_4 . Shifting of the peaks with the increase of vanadium concentration, however, can be observed. This can be understood since there would be lattice mismatch due to vanadium insertion into the crystal structure of LiFePO_4 . The shifting of the lattice parameters implies that vanadium doping has been successfully occupied the sites of Fe^{2+}

in the LiFePO_4 structure to form solid solution of $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4$

Morphology and Particle Distribution

SEM characterization was carried out in order to evaluate the effect of vanadium doped on the morphology and particle size distribution of $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4$. According to the SEM images in Figure 4, it can be observed that LiFePO_4 powders are mainly fine particles between 0.5 μm and 2 μm sizes. Some of pure LiFePO_4 particles form agglomeration structure with the hexagonal look shaped particles.

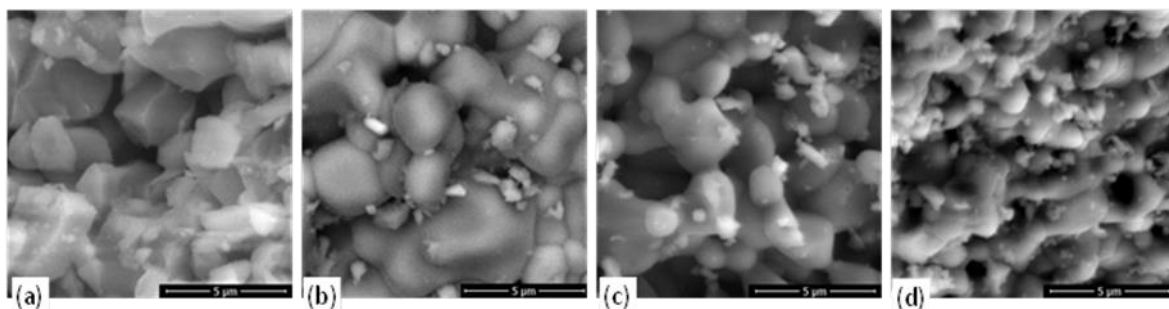


Figure 4. Secondary electron images of the as-synthesized LiFePO₄/C with (a) 0 wt.% vanadium, (b) 3 wt.% vanadium, (c) 5 wt.% vanadium, and (d) 7 wt.% vanadium. Bar scale is 5 μm

The LiFePO₄ with 3 wt.% vanadium shows decrease in agglomeration and particle changes to be more spherical in shape. For the vanadium 5 wt.% and 7 wt.% doped LiFePO₄, the morphology shows spherical shaped particles and less agglomerate. It is worth to note that the particle size gets smaller with the increase of vanadium concentration. This result is agreement with the finding from others (Y. Zhang et al. 2012). This also implies that vanadium doping has a great effect on the structure of LiFePO₄ particles and expected to

be beneficial to the enhancement of LiFePO₄ electronic conductivity (Y. Zhang et al. 2012).

For qualitative purpose, Figure 5 shows Energy Dispersive X-Ray Spectroscopy (EDS) results from the as-prepared sample and the one containing vanadium. As seen in Figure 5a, the sample has the basic elements of C, Fe, P, and O, which indicated the presence of LiFePO₄ compound in the structure coated by carbon, whereas the presence of vanadium shown in Figure 5b, 5c, and 5d reveal that the vanadium is already distributed in LiFePO₄.

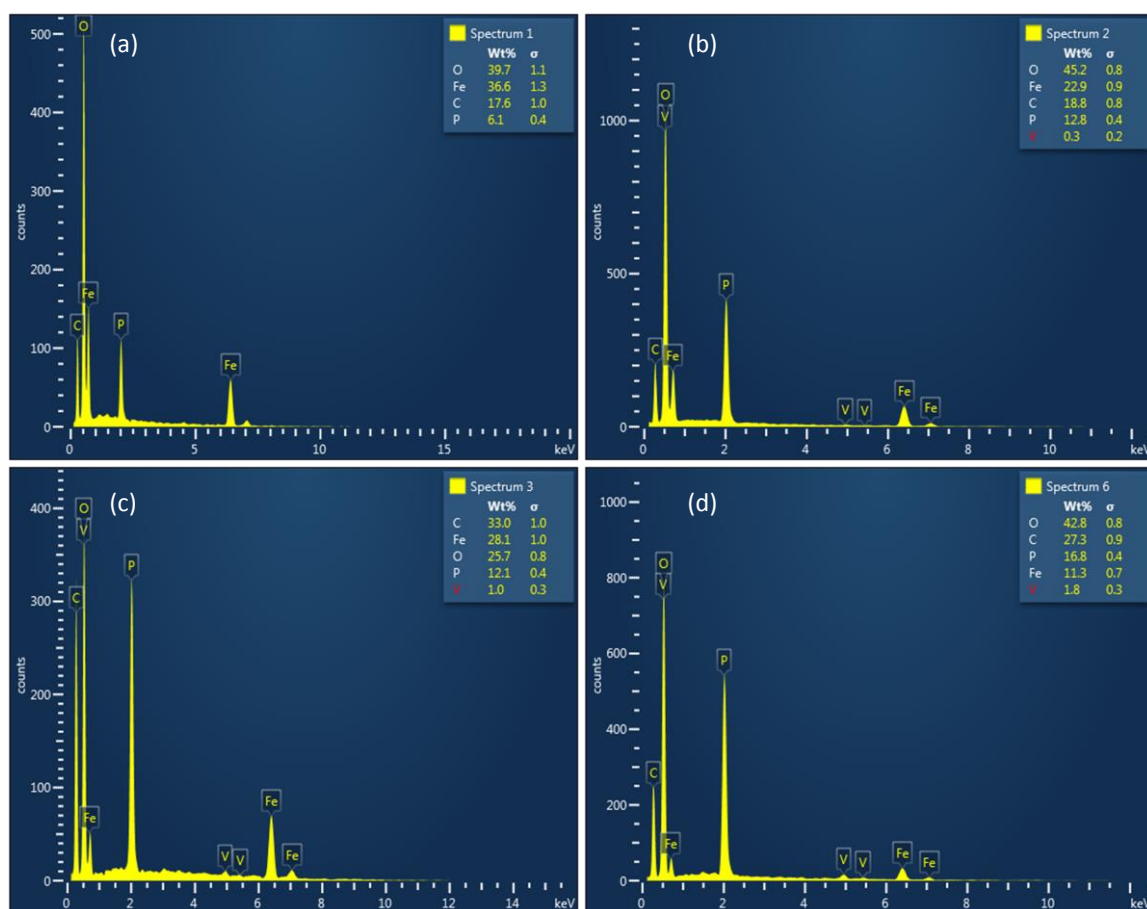


Figure 5. Energy dispersive X-ray spectroscopy of the sample showing the basic elements of C, Fe, P, and O for 0 wt.% vanadium (a) C, Fe, P, O, and V for 3 wt.%, (b) 5 wt.%, (c) 7 wt.%, and (d) vanadium

Conductivity and Battery Performance

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out to explore the effect of vanadium doping and bamboo activated carbon coating on the electrochemical performance of the LiFePO_4 cathode. The results are given in Figure 6 in the forms of Nyquist plot. As seen in Figure 6, the values of the cross point of the semicircle on the horizontal axes represent the charge transfer resistance. The straight line represents the Warburg impedance, which is associated with the lithium ion diffusion in the inner of LiFePO_4 particles. In this instance, charge transfer resistance has a close relationship between composition and conductivity of the interface. Pure LiFePO_4 has very low conductivity ($\sim 10^{-9}$ S/cm) (Chung, Bloking, and Chiang 2002). As shown in Figure 6, bamboo activated carbon coated only LiFePO_4 (LFP 0% V) has increased in the conductivity of about 1.25×10^{-5} S/cm. This indicates that bamboo activated carbon coating can decrease the resistance and increase the conductivity of LiFePO_4 . Doping with vanadium even increases the conductivity of LiFePO_4 . As the vanadium levels increases, each for 3 wt.%, 5 wt.%, and 7 wt.%, the conductivity increases 2.02×10^{-5} S/cm, 4.37×10^{-5} S/cm, and 5.69×10^{-5} S/cm, respectively. The vanadium doped sample shows superior electrochemical performance than the undoped sample due to higher conductivity and better electrode kinetics related to the synergistic effect of V^{3+} in the

lattice (Pietrzak et al. 2013).

Cyclic voltammetry and charge/discharge measurements were performed for the two active materials only, i.e. LiFePO_4/C at 3 wt.% and 7 wt.% vanadium to represent the active materials with the lowest and the highest conductivity, respectively. The graphs are given in Figure 7. As seen in Figure 7, cyclic voltammetry curves shown at the top have reduction-oxidation peaks at 3.70 volts and 3.10 volts for 3 wt.% vanadium (top left) and at 3.60 volts and 3.20 volts for 7 wt.% vanadium (top right), respectively. The charge/discharge testing was performed at the potential range of 2.5 V until 4.2 V at two capacities, i.e. 0.5C and 4C. The obtained curves are shown at the bottom in Figure 7 for the LiFePO_4/C at 3 wt.% vanadium (bottom left) and 7 wt.% vanadium (bottom right). The initial charge and discharge capacity at 0.5C for LiFePO_4/C at 7 wt.% vanadium (8.0 mAh/g) is higher than that of 3 wt.% vanadium (4.2 mAh/g). At 4C however, the charge and discharge capacity of 7 wt.% vanadium drops to around 4.0 mAh/g, whereas for LiFePO_4/C at 3 wt.% vanadium drops to around 1.0 mAh/g. This can be understood since at high vanadium concentration, at low cycle it can accommodate high capacity. At high cycle, however, the uneven presence of vanadium and carbon and the presence of pores might start forming a bulk layer that blocks and decreases the electrical conductivity and thus the capacity.

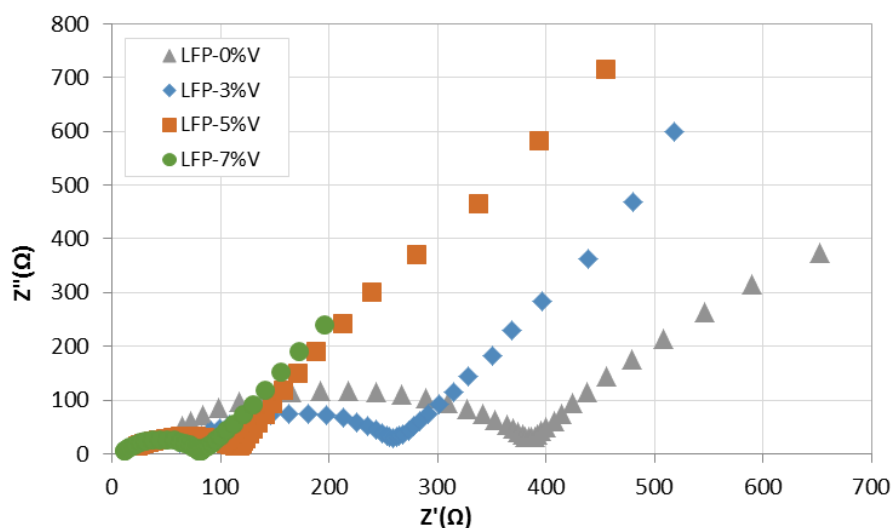


Figure 6. Nyquist plots of LiFePO_4/C (grey triangle), 3 wt.% (blue diamond), 5 wt.% (orange square), and 7 wt.% (green circle) vanadium

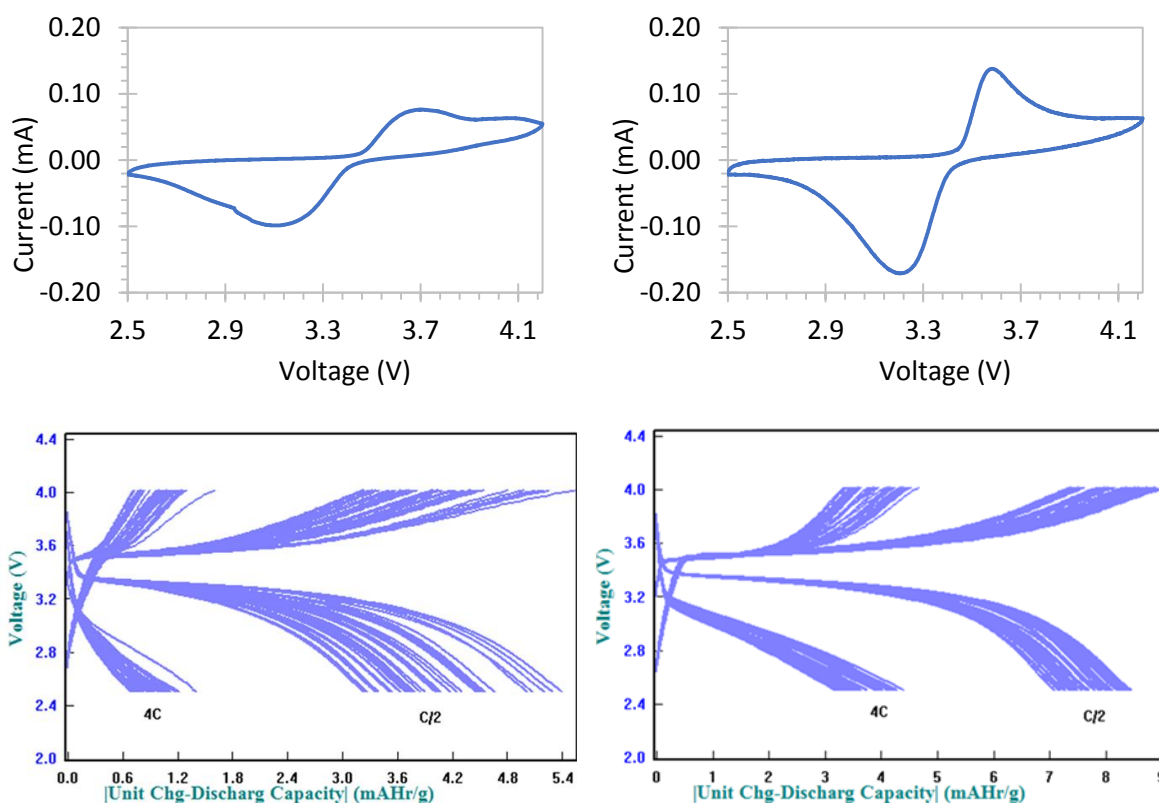


Figure 7. Cyclic voltammetry (top) and charge discharge (bottom) testing results of 3 wt.% (left) and 7 wt.% (right) vanadium

This current result is promising in terms of improving the conductivity of LiFePO_4 for lithium ion battery cathode using cheap natural resources of activated carbon. In comparison to other works, Bhardwaj et al. (2007) have used bamboo carbon for lithium ion battery anode instead of using it to improve the conductivity of LiFePO_4 cathode with a capacity of 130 mAh/g. Gu et al. (2015) have also used bamboo biochar for lithium-sulfur batteries with a capacity of up to 550 mAh/g. Their results can be understood since they used the bamboo carbon for different purposes. Nonetheless, compared to our previous results on the use of activated carbon pyrolyzed from rice husk (Sofyan, Sekaringtyas, et al. 2018) and coconut shells (Sofyan, Rachmawati, et al. 2018) for the same purpose on improving the conductivity of LiFePO_4 , the performance of this current result is much better.

CONCLUSION

In this study, activation process of bamboo charcoal was successful using H_3PO_4 reagent and produce a good crystallinity of activated carbon that can increase the conductivity of LiFePO_4 from 10^{-9} S/cm to 1.25×10^{-5} S/cm. Doping with vanadium even increases the conductivity of LiFePO_4 in which for 3 wt.%, 5 wt.%, and 7 wt.% vanadium, the conductivity increases 1.246×10^{-5} S/cm,

2.020×10^{-5} S/cm, 4.371×10^{-5} S/cm, and 5.688×10^{-5} S/cm, respectively. At 0.5C, the initial charge and discharge capacity for LiFePO_4/C at 7 wt.% vanadium is 8 mAh/g. This value is higher than that of 3 wt.% vanadium (4.2 mAh/g). At 4C however, the charge and discharge capacity of 7 wt.% vanadium drops to around 4 mAh/g, whereas for LiFePO_4/C at 3 wt.% vanadium drops to around 1 mAh/g.

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